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Scientific Paper

A STUDY OF THE CORROSION INHIBITION OF CARBON-STEEL IN DILLUTED AMMONIA MEDIA USING 2-MERCAPTO-BENZOTHIAZOL (MBT)

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Abstract

The inhibiting effect of MBT has been studied regarding the corrosion of carbon-steel in diluted ammonia solution at room temperature. The effects of the inhibitor have been demonstrated using weight loss and electrochemical measurements. The increase of the inhibitor concentration leads to a decrease in the corrosion rate and in the corrosion current. The microscopic analysis of the surface of the electrode shows a decrease of the corrosion spots with the increase of the MBT concentration. This indicates a good adsorbability of MBT on the metal surface. Mössbauer spectrometry shows the formation of a superficial film on the surface of the corroded sample in the presence of MBT. This film provides a good corrosion protection for the sample.

Key words: carbon-steel, ammonia media, inhibitor, MBT, Mössbauer spectrometry

Introduction

In order to improve the corrosion protection numerous advanced treatments, including organic compounds,[1-10] have been proposed. The inhibition efficiency of the organic compounds is closely related to the structure and the properties of the film formed on the metal surface. For the inhibition of the carbon-steel corrosion in different media there have been used organic compounds containing sulphur and azote. The results show that most inhibitors act through adsorption on the metal surface.[11-17] The carried out studies show that adsorption depends especially on the chemical structure of the inhibitor, on the nature, surface and the composition of the steel[5] as well as on the strength of the inhibitor-metal bond.

MBT has been studied in hydrochloric acid solutions, for the protection of carbon-steel and iron, using the concentration of 1%.[18,19] Recent investigations show that MBT offers a satisfactory protection in 1M hydrochloric acid mediums, at a concentration of

500 ppm.[20] MBT has also given good results in aqueous solutions of nitrogen-ammonium. For the solution of 62.5% NH_4NO_3 and 23.7% NH_3, at the same penetration index, an efficiency of 89% has been reported for concentrations of MBT from 125 to 500 ppm.[21] Investigations prove the fact that the water containing ammonia-ammonium used in the cooling circuits, especially the ones used in the industry of fertilizers based on ammonium, have a negative corrosive impact on pipes.[22,23]

The present study demonstrates the role of MBT in enhancing the passive film formation, in the case of the general corrosion of carbon-steel in a slightly alkaline medium which contains 10^{-3} M NH_3. The efficiency of the inhibitor was determined using weight loss and electrochemical measurements. The capacity of adsorption of MBT on the surface of carbon-steel was studied using the Mössbauer spectrometry and the microscopic examination of the samples.

Results and discussions

Weight loss measurements

The corrosion rate was expressed by the gravimetric index k_g (g/m^2·day). For the carbon-steel samples the weight losses were determined in a 10^{-3} M ammonia solution, in the absence and in the presence of variable concentrations of MBT, at room temperature, in a closed system, for 5 days. The determinations of weight losses are presented as general corrosion rate in Figure 1a. The inhibition efficiency, expressed in percentage P, was calculated by means of the following relation:

$$P = \frac{k_{g0} - k_g}{k_{g0}} \cdot 100$$

k_{g0} = the corrosion rate in the absence of the inhibitor (mg/m^2·day)

k_g = the corrosion rate in the presence of the inhibitor (mg/m^2·day)

The inhibition efficiency, calculated by weight loss measurements, under the given experimental conditions, is presented in Figure 1b. The increase in MBT concentration leads to a decrease in the corrosion rate. The presence of MBT delays the general corrosion of the samples. This suggests the inhibition of carbon-steel corrosion in 10^{-3} M ammonia solution, in the presence of MBT, is due to the adsorption of the latter on the metal surface.

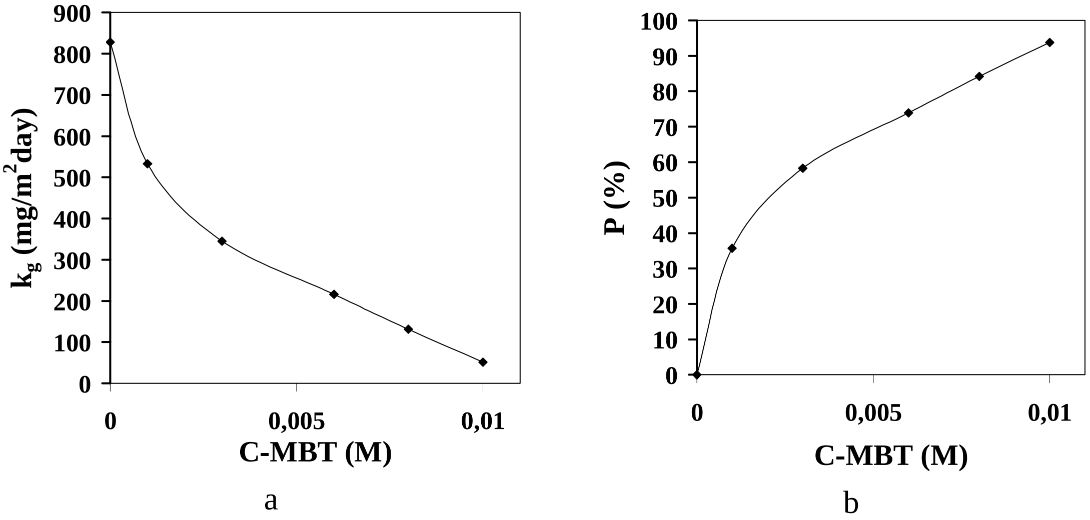

Figure 1: (a) Variation of the corrosion rate with MBT concentration for the carbon-steel samples in 10^{-3} M ammonia solution; (b) Variation of the inhibition efficiency with MBT concentration, expressed in percentage (P), for the corroded carbon-steel sample in a 10^{-3} M ammonia solution.

It has been observed that in the presence of a concentration of 10^{-2} M MBT in a 10^{-3} M ammonia solution, the efficiency is approximately 94%, which proves a very good adsorbability on the carbon-steel's surface.

It can also be assumed that there occurs formation of complexes between MBT and different metal cations, which are found in the steel's structure. These complexes can form stable passive films on the steel's surface, decreasing the corrosion rate.

Electrochemical measurements

The effect of the inhibitor has been studied by the anodic and cathodic galvanostatic polarization of the carbon-steel sample in a 10^{-3} M ammonia solution, both in the presence and absence of MBT. The anodic and cathodic polarization curves are presented in Figure 2.

Five determinations were made for each solution, taking into consideration the most reproducible responses for the same current densities. In this study, the minimum recorded current was 10 µA. Thus E_{cor} was defined as the potential from which a current larger than 10 µA was observed.

The anodic polarization of steel electrodes in the inhibitor containing 10^{-3} M ammonia solution is shifted to less negative values, while the cathodic polarization shifts to more negative values with increasing current density. The presence of organic inhibitors in the corrosive medium increases the anodic and cathodic overpotentials and decreases the corrosion current (i_{cor}). These changes increase with increasing inhibitor concentration. This behaviour supports the inhibition function of these organic compounds. Decrease of the corrosion current (i_{cor}) was associated with an appreciable shift of corrosion potential (E_{cor}) to a less negative value. This suggests that although inhibition is of mixed type, it is predominantly anodic.

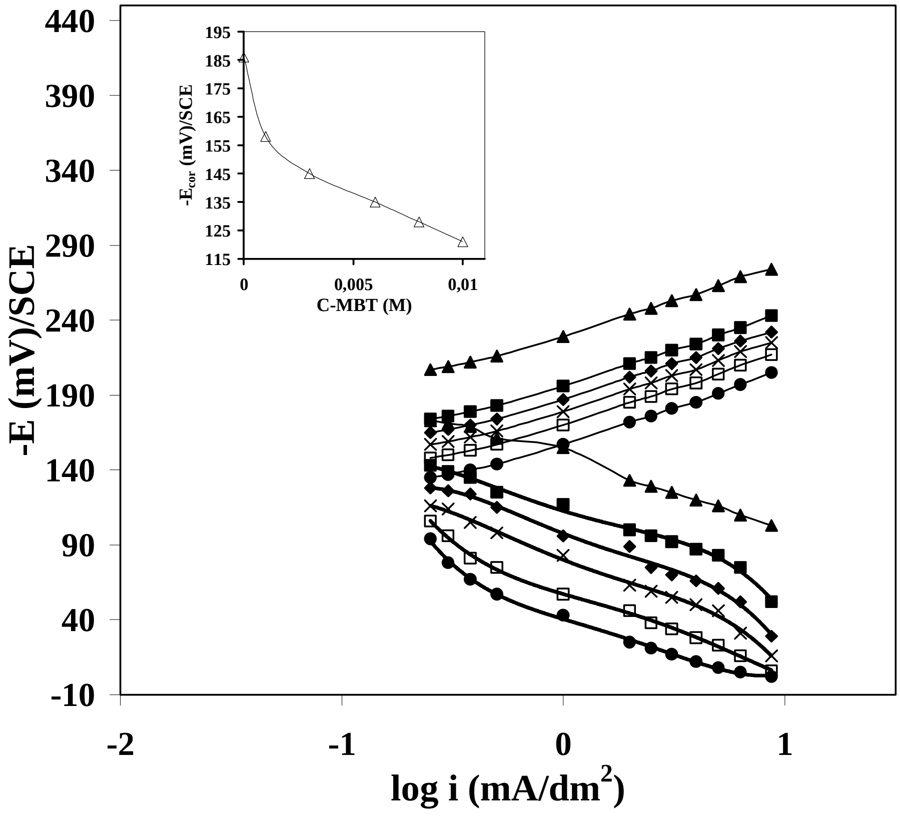

Figure 2. (—△—) Dependence of E_{cor} on C-MBT (M) and the polarization curves of carbon-steel samples in a 10^{-3} M ammonia solution in the presence of MBT with different concentrations: (—▲—)0; (—■—)10^{-3} M; (—◆—)$3\cdot10^{-3}$; (—×—)$6\cdot10^{-3}$; (—□—) $8\cdot10^{-3}$ M and (—●—)10^{-2} M.

The percentage inhibition efficiency (P) of these inhibitors was also determined from the polarization measurements according to the equation:

$$P = \frac{i'_{cor} - i_{cor}}{i'_{cor}} \cdot 100$$

where i'_{cor} and i_{cor} are the inhibited and uninhibited corrosion current density, respectively, obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential. In the presence of the inhibitor, the steel is active and dissolves by a Tafel slope of 43 ± 1 mV. The slopes in the cathodic Tafel segments are less than 2.303 RT/βF (β = 0.5). This is determined by the cathodic reduction of all the components, namely, O_2, NH_4^+. The reduction of water molecules is probably an additional cathodic process. Metal ionization is suppressed by the inhibitor more strongly (Figure 2) than the cathodic process is stimulated, and the free corrosion potential of steel becomes significantly higher with an increase in C-MBT (Figure 2). The results are presented in Table 1.

Table 1. The electrochemical parameters for the carbon-steel sample in absence and presence of MBT in a 10^{-3} M ammonia solution and the percentage P obtained by the weight loss measurements and the galvanostatic polarization.

MBT concentration (M)	E_{cor} (mV) /SCE	i_{cor} (µA/dm^2)	P (%)	
			From weight loss measurements	From Tafel polarization
0	-186	116	-	-
10^{-3}	-158	82	35.7	29.3
$3\cdot10^{-3}$	-145	57	58.3	51
$6\cdot10^{-3}$	-136	36.7	73.9	68.3
$8\cdot10^{-3}$	-128	22.2	84.2	80.8
10^{-2}	-121	13	93.8	89

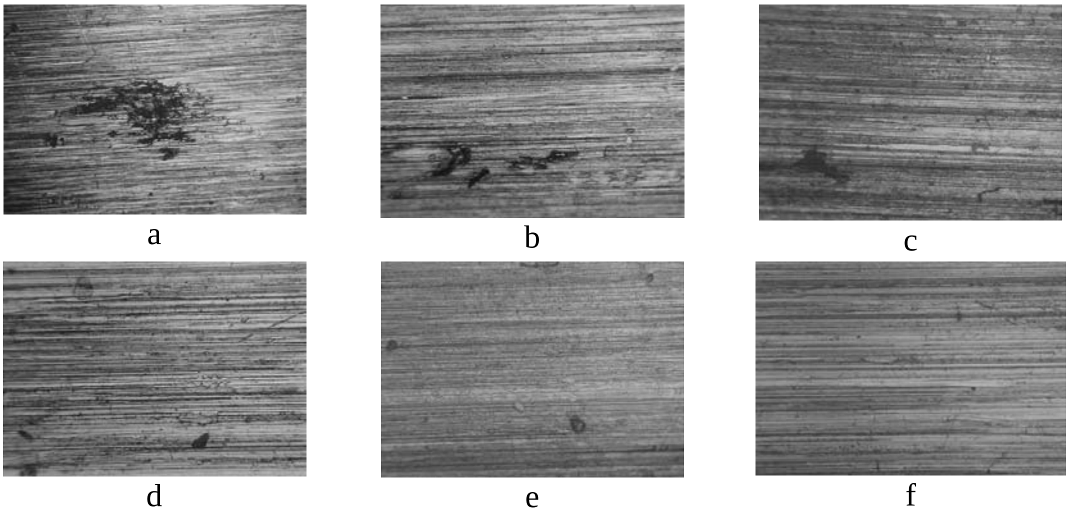
a b c
d e f

Figure 3: The electrodes' surfaces microscopically analyzed (X1000).

It can be observed that the inhibition efficiency calculated from the weight loss measurements is close to that calculated from electrochemical measurements, especially at high concentrations of inhibitor.

The surface analysis of the electrochemically corroded samples was made under a microscope. In absence of the inhibitor the experimental results show that the surface of carbon-steel was covered with a large number of corrosion spots, as shown in Figure 3a. In the presence of MBT the corrosion spots reduce in intensity concomitantly with the increase of the inhibitor concentration (figures 3b-3f). Thus, at a MBT concentration of 10^{-2} M no corrosion spots are observed.

Mössbauer spectrometry

The electrochemically-corroded carbon-steel samples in a 10^{-3} M ammonia solution without MBT and in a 10^{-3} M ammonia solution with 10^{-2} M MBT were also tested using the Mössbauer surface analysis. This analysis indicates the formation of a superficial film on the surface of the corroded electrode in the presence of MBT, which gives it a very good passivation.

The CEMS spectra of the sample corroded in solution with 10^{-3} NH_3 concentration are shown in Figure 4. The best fit of the CEMS spectra for the corroded samples uses an addition Fe^{3+} paramagnetic doublet to the sextet.

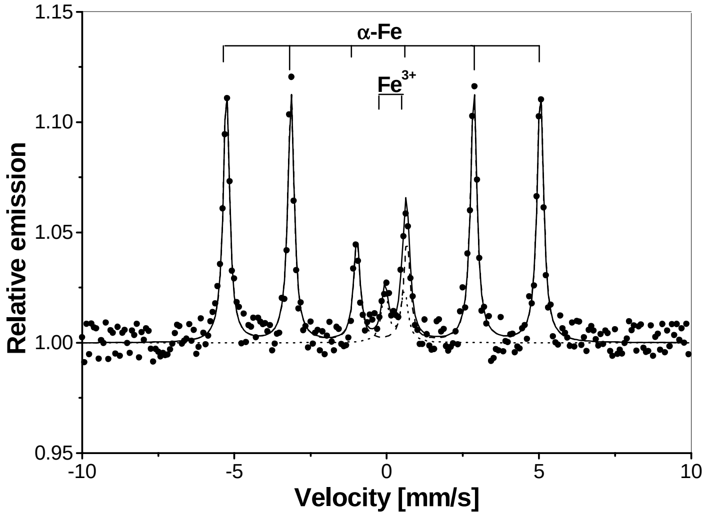

Figure 4. CEMS spectrum of a corroded sample in a solution with 10^{-3} NH_3 concentration (• data; — fit; ···· Fe^{3+}; --- α-Fe).

The parameters of the sextet (hyperfine magnetic field, quadrupole splitting, isomer shift, line width) are almost identical to those of the uncorroded sample. We note though the increase of the isomer shift to the value of 0.02 mm/s ± 0.02 as well as the continuous decrease of the hyperfine magnetic field value. The hyperfine magnetic field's value drops from 26.308×10^6 A/m ± 0.199×10^6 (330.6 KOe ± 2.5) to 26.054×10^6 A/m ± 0.199×10^6 (327.4 KOe ± 2.5). This latter value, in connection with a slight change of the isomer shift can be explained by the presence of the carbon's impurities.

This demonstrates that in the process of corrosion there is a certain preference for the positions of the iron, which are close to the atoms of the alloying elements. We note the tendency of decreasing regarding the width of the sextet's lines: from 0.26 mm/s (the case of the uncorroded sample) down to 0.25 mm/s. The preferential orientation of magnetic moments in the sample plane continues to exist even after the corrosion of the sample. The main difference between the corroded sample's sextets and the uncorroded sextets consists of the decrease of the intensity lines.

This demonstrates the presence of a superficial layer on corroded samples'surface. The relative area of the doublet increases at 8% ± 3 for the corroded sample. This reconfirms the formation of a superficial compound, without magnetic ordering, as a result of corrosion. The quadrupole splitting value of the doublet is in the range 0.62 mm/s ± 0.03 while the isomer shift values increase to 0.42. These parameters show the presence of Fe^{3+} and are similar to those shown by amorphous Fe^{3+} oxyhydroxides,[24] superparamagnetic α-FeOOH and/or γ-FeOOH[25-27] and Fe $(OH)_3$.[28] The assignment of this doublet to a specific chemical species is difficult solely on the basis of the Mössbauer data obtained at room temperature. Small relative areas of the doublet, as well as its parameters are showing the initial stage of the corrosion. In this stage we believe the main product of the corrosion is an amorphous Fe^{3+} oxyhydroxide with a non-stoichiometric composition.

In Figure 5 the CEMS spectrum of the sample after corrosion process in the presence of the MBT inhibitor is presented. The best fitting of the TMS spectrum shows the presence of a single sextet. The parameters of this singlet are practically the same as for a α-Fe sample. The full width at half-height of the outermost lines (0.3 mms^{-1} ± 0.01) confirms the low concentration of an alloying elements given by chemical analysis. The main difference between the corroded sample's sextets, in the presence of the MBT inhibitor, and the uncorroded sextets consists of the decrease of the intensity lines. This demonstrates the presence of a superficial layer on corroded samples' surface.

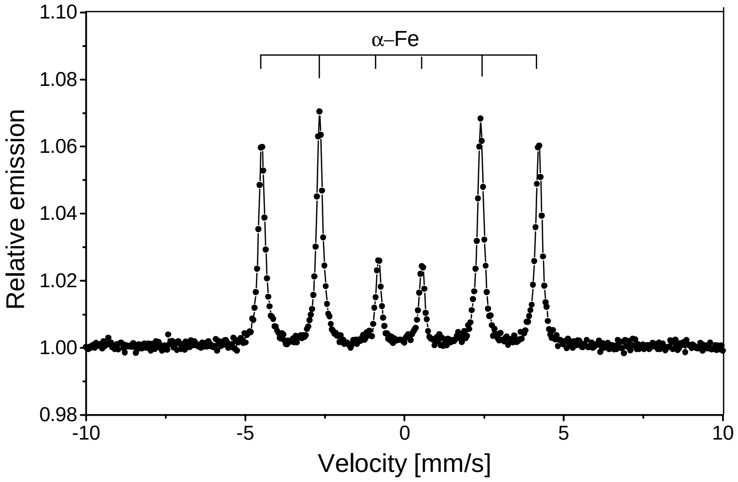

Figure 5. CEMS spectrum of a corroded sample in a solution with 10^{-3} NH_3 concentration with 10^{-2} M MBT (• data; — fit; ···· Fe^{3+}; --- α-Fe).

In all the CEMS spectra, the intensities of the second and fifth peaks of the α-Fe spectrum with regard to the third and fourth peaks shows that the directions of the γ-ray and the magnetic moments are nearly perpendicular. There is a magnetic anisotropy on the surface of the samples, obtained, mainly, by polish procedure. In contrast TMS spectra show that in the interior of the sample the magnetic moments are in a random arrangement. The line width of the CEMS spectrum is 0.27 mms^{-1} ± 0.02. A smaller line width is expected in the backscattering geometry due to lack of saturation broadening.

Conclusions

MBT behaves as a corrosion inhibitor for carbon-steel in a 10^{-3} M ammonia solution. Corrosion was investigated by means of weight loss and electrochemical measurements. The samples' surfaces analysis was carried out microscopically and using the Mössbauer spectrometry. The increase of the inhibitor concentration leads to a decrease in the corrosion rate and in the corrosion current. The microscopic analysis shows that the corrosion spots reduce in intensity concomitantly with the increase in MBT concentration, which demonstrates that the latter acts as an adsorption inhibitor on the steel's surface.

The Mössbauer measurements indicate the existence of a superficially adhered film, which gives good protection to electrodes, indicating, probably, that the formation of complexes is also possible between the MBT molecules and the metal cations which are found in steel's composition, giving it a good passivation.

Experimental

Weight loss measurements

Experimental determinations focused on calculating the corrosion rate of carbon-steel through weight loss measurements in diluted ammonia solutions, both in the absence and in the presence of MBT as an inhibitor. The carbon-steel that was used had the following composition: C=0.15%; Mn=0.4%; Si=0.25%; S=0.25% and Fe up to 100%. For these weight loss measurements, the metal samples, with an active surface of 8 cm^2, were mechanically polished, degreased with ethyl alcohol and chemically uncapped with a solution of HCl 5%. Then the samples were washed in double-distilled water and dried in warm air. The experiments were made in 10^{-3} M ammonia solution without an inhibitor and in the presence of MBT at different concentrations: 10^{-3} M, $3\cdot10^{-3}$, $6\cdot10^{-3}$, $8\cdot10^{-3}$ M, and 10^{-2} M. The samples were kept in the respective media in a closed system for 5 days at room temperature. The corrosion products were removed as soon as the samples were taken out of the aggressive solutions, by washing them in a 5% HCl solution with an inhibitor, in warm medium then degreased in alcohol and dried in warm air.

Electrochemical measurements

For the study of polarization a standard corrosion cell was used with a working electrode made of carbon-steel with an active surface of 4 cm^2. The saturated calomel electrode (SCE) was used as a reference electrode. The auxiliary electrode was a carbon-steel plate identical to the one used as the working electrode. The carbon steel electrodes were made of the same material as the plates used for weight loss measurements.

The electrochemical measurements were carried out using a Keithley 2420 3A Source Meter, and the data were computerized. The morphology of steel’s surface before and after being treated with MBT was examined with a JEOL JSMT 200 microscope.

Mössbauer spectrometry

Mössbauer spectroscopy was performed at room temperature in the transmission (TMS) and conversion electron spectroscopy (CEMS) using a Wissel constant-acceleration spectrometer with a ^{57}Co-Rh source. The CEMS measurements, effected with CEMS detector RiKon-5, were conducted to a high degree of accuracy, ensuring the same geometry of the detection space and same gas flow rate for all the samples. The parameters of the Mössbauer spectra were calculated using a computer-fitting program which assumes a Lorentzian line shape. The isomer shifts were reffered to α-Fe.

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Povzetek

Študiran je bil inhibitorski efekt MBT na korozijo ogljikovega jekla v raztopini razredčenega amoniaka pri sobni temperaturi. Efekt inhibitorja je bil demonstriran z izgubo mase in elektrokemijskimi meritvami. Povečanje koncentracije inhibitorja vodi k zmanjšanju hitrosti korozije. Mikroskopska analiza površine elektrode kaže zmanjšanje korozivnih področij ob povečanju koncentracije MBT.